

FORM PTO-1390 (REV. 9-2001)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER Mo-6753/LeA 33,677	
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				U.S. APPLICATION NO. (If known, see 37 CFR 1.5) <div style="font-size: 24pt; font-weight: bold; text-align: center;">09/980882</div> To Be Assigned	
INTERNATIONAL APPLICATION NO. PCT/EP00/03618		INTERNATIONAL FILING DATE 20 April 2000 (20.04.00)		PRIORITY DATE CLAIMED 06 May 1999 (6.05.99)	
TITLE OF INVENTION DIENE RUBBERS CONTAINING CARBOXYL GROUPS					
APPLICANT(S) FOR DO/EO/US					
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:					
<ol style="list-style-type: none"> 1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. 2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. 3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below. 4. <input checked="" type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31). 5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) <ol style="list-style-type: none"> a. <input checked="" type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau). b. <input type="checkbox"/> has been communicated by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). 6. <input checked="" type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)). <ol style="list-style-type: none"> a. <input checked="" type="checkbox"/> is attached hereto. b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4). 7. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) <ol style="list-style-type: none"> a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau). b. <input type="checkbox"/> have been communicated by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input type="checkbox"/> have not been made and will not be made. 8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)). 9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). 10. <input type="checkbox"/> An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). 					
Items 11 to 20 below concern document(s) or information included:					
<ol style="list-style-type: none"> 11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. 12. <input checked="" type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. 13. <input checked="" type="checkbox"/> A FIRST preliminary amendment. 14. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. 15. <input type="checkbox"/> A substitute specification. 16. <input type="checkbox"/> A change of power of attorney and/or address letter. 17. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825. 18. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4). 19. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4). 20. <input checked="" type="checkbox"/> Other items or information: 					
Form PTO 1449 w/references					

To Be Assigned

09/980882 PCT/EP00/03618

ATTORNEY'S DOCKET NUMBER

Mo-6753/LeA 33,677

21. ☒ The following fees are submitted:**BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):**

Neither international preliminary examination fee (37 CFR 1.482)

nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO

and International Search Report not prepared by the EPO or JPO. \$1040.00

International preliminary examination fee (37 CFR 1.482) not paid to
USPTO but International Search Report prepared by the EPO or JPO \$890.00International preliminary examination fee (37 CFR 1.482) not paid to USPTO
but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$740.00International preliminary examination fee (37 CFR 1.482) paid to USPTO
but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$710.00International preliminary examination fee (37 CFR 1.482) paid to USPTO
and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00**ENTER APPROPRIATE BASIC FEE AMOUNT =****CALCULATIONS PTO USE ONLY**

\$ 890.00

\$ 0.00

Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(e)).

CLAIMS NUMBER FILED NUMBER EXTRA RATE

Total claims 5 - 20 = 0 x \$18.00 \$ 0.00

Independent claims 4 - 3 = 1 x \$84.00 \$ 84.00

MULTIPLE DEPENDENT CLAIM(S) (if applicable) + \$280.00 \$ 0.00

TOTAL OF ABOVE CALCULATIONS =

\$ 974.00

☐ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above
are reduced by 1/2. + \$ 0.00**SUBTOTAL =**

\$ 974.00

Processing fee of \$130.00 for furnishing the English translation later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(f)). \$ 0.00**TOTAL NATIONAL FEE =**

\$ 974.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be
accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property + \$ 40.00**TOTAL FEES ENCLOSED =**

\$ 1,014.00

Amount to be
refunded: \$

charged: \$

a. ☐ A check in the amount of \$ _____ to cover the above fees is enclosed.b. ☒ Please charge my Deposit Account No. 13-3848 in the amount of \$ 1,014.00 to cover the above fees.
A duplicate copy of this sheet is enclosed.c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any
overpayment to Deposit Account No. 13-3848. A duplicate copy of this sheet is enclosed.d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card
information should not be included on this form.** Provide credit card information and authorization on PTO-2038.**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR
1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO.

SIGNATURE

Noland J. Cheung

NAME

39,138

REGISTRATION NUMBER

09/980882

JC10 Rec'd PCT/PTC 0 2 NOV 2001

PATENT APPLICATION
Mo6753
LeA 33,677

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN APPLICATION OF)
THOMAS SCHOLL ET AL) PCT/EP 00/03618
SERIAL NO.: TO BE ASSIGNED)
FILED: HEREWITH)
TITLE: DIENE RUBBERS CONTAINING)
CARBOXYL GROUPS)

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Upon the granting of a Serial Number and Filing Date and prior to the examination of the subject application, kindly amend the Specification and Claims as follows:

"Express Mail" mailing label number ET700176899US
Date of Deposit November 2, 2001

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner of Patents and Trademarks, Washington, D.C. 20231

Donna J. Veatch

(Name of person mailing paper or fee)


Signature of person mailing paper or fee)

IN THE SPECIFICATION:

Kindly replace the Title of the Invention with the following:

-- DIENE RUBBERS CONTAINING CARBOXYL GROUPS --.

IN THE ABSTRACT

Please replace page 16, a page containing an abstract with the enclosed page that contains a revised Abstract of the Disclosure. A separate page is enclosed herewith.

--DIENE RUBBERS CONTAINING CARBOXYL GROUPS

ABSTRACT OF THE DISCLOSURE

The present invention relates to rubber mixtures containing diene rubber with a concentration of carboxyl groups of 0.1 to 2 wt.% and a glass transition temperature of -120 to -50°C and their mixtures with fillers, optionally further rubbers and rubber auxiliary substances and vulcanisates prepared therefrom. Rubber mixtures according to the invention are suitable for producing highly reinforced, abrasion-resistant moulded items, in particular for producing tire treads which have a particularly high resistance to wet skidding, a high abrasion resistance and a low rolling resistance and also for tire sidewalls with especially good fatigue resistance.--

On page 1, line 3, kindly insert the following:

-- FIELD OF THE INVENTION --.

On page 1, line 12, kindly insert the following:

--BACKGROUND OF THE INVENTION--.

On page 2, line 11, kindly insert the following:

-- SUMMARY OF THE INVENTION --.

On page 11, line 1, kindly insert the following:

--Table 1--.

On page 11, kindly replace Table 1 with the following new Table 1.

--Table 1

	Comparison 2.A	Example 2.1
in the kneader mixed:		
Buna VSL 5025-1 (37.5 phr mineral oil extended L-SBR, Bayer AG)	61.9	61.9
natural rubber	10	10
polybutadiene rubber Buna CB 45 (Bayer)	45	0
carboxylic group containing BR according example 1 (20 phr oil content)	0	54
mineral oil Enerthene 1849-1 (BP)	20	11
silica Vulkasil S (Bayer AG)	70	70
silane Si (69 (Degussa Hüls)	6	6
carbon black Corax N121 (Degussa Hüls)	10	10
zinc oxide	3	3
stearic acid	1	1
protective wax Antilux 654 (Rheinchemie)	1.5	1.5
antioxidant Vulkanox HS (Bayer AG)	1	1
antioxidant Vulkanox 4020 (Bayer AG)	1	1

On the mill admixed

N-cyclohexylmercaptobenzthiazolsulfenamide		
Vulkacit CZ (Bayer AG)	1.8	1.8
diphenylguanidine Vulkacit D (Bayer AG)	2	2
sulfur	1.5	1.5

--

On page 12, line 1, kindly insert the following:

-- Table 2 --.

On page 12, kindly replace Table 2 with the following new Table 2.

[illegible]

—

IN THE CLAIMS:

Kindly cancel Claims 1 - 5.

Kindly add the following new Claims:

- 6. A rubber mixture comprising one or more rubbers with 0.1 to 2 wt.% of bonded carboxyl groups or their salts and a glass transition temperature in the range from -120° to -50°C and one or more fillers in the range 10 to 500 parts by wt., with respect to 100 parts by wt. of rubber.
7. A rubber mixture according to Claim 1, wherein said rubber is formed from diolefins.
8. A process for preparing a rubber with 0.1 to 2 wt.% of bonded carboxyl group comprising the step, after polymerization in solution, of reacting rubber with carboxylmercaptans of the general formula (I)



in which

R¹ represents a linear, branched or cyclic C₁-C₃₆ alkylene group, which may optionally be substituted with up to 3 further carboxyl groups, or which may be interrupted by nitrogen, oxygen or sulfur atoms, or a C₆-C₁₂-arylene group

and

X represents hydrogen or a metal or ammonium ion,

optionally in the presence of radical starters.

9. Molded items comprising rubber mixtures which comprise one or more rubbers with 0.1 to 2 wt.% of bonded carboxyl groups or their salts and a glass transition temperature in the range from -120° to -50°C and one or more fillers in the range 10 to 500 parts by wt., with respect to 100 parts by wt. of rubber.
10. Tires comprising rubber mixtures which comprise one or more rubbers with 0.1 to 2 wt.% of bonded carboxyl groups or their salts and a glass transition temperature in the range from -120° to -50°C and one or more fillers in the range 10 to 500 parts by wt., with respect to 100 parts by wt. of rubber. --.

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REMARKS

The Applicants respectfully request the Preliminary Amendment be entered as the amendment places the claims as well as the Specification in proper form.

New Claims 6 - 10 replace now cancelled Claims 1 - 5. New Claims 10 and 11 replaces the use claim of now cancelled Claim 5. The Applicants respectfully submit that no new matter is added.

Respectfully submitted,

By



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s/rmc/njc0105

VERSION WITH MARKINGS TO SHOW CHANGES MADE

IN THE SPECIFICATION: (Marked-Up)

The following are changes and additions made to the specification.

Kindly replace the Title Of The Invention with the following:

[CARBOXYL GROUP-CONTAINING] DIENE RUBBERS CONTAINING CARBOXYL GROUPS.

IN THE ABSTRACT

Please replace page 16, a page containing an abstract with the enclosed page that contains a revised Abstract of the Disclosure. A separate page is enclosed herewith.

--DIENE RUBBERS CONTAINING CARBOXYL GROUPS--

ABSTRACT OF THE DISCLOSURE

The present invention relates to rubber mixtures containing diene rubber with a concentration of carboxyl groups of 0.1 to 2 wt.% and a glass transition temperature of -120 to -50°C and their mixtures with fillers, optionally further rubbers and rubber auxiliary substances and vulcanisates prepared therefrom. Rubber mixtures according to the invention are suitable for producing highly reinforced, abrasion-resistant moulded items, in particular for producing tire treads which have a particularly high resistance to wet skidding, a high abrasion resistance and a low rolling resistance and also for tire sidewalls with especially good fatigue resistance.--

On page 1, line 3, kindly insert the following:

FIELD OF THE INVENTION

On page 1, line 12, kindly insert the following:

BACKGROUND OF THE INVENTION

On page 2, line 11, kindly insert the following:

SUMMARY OF THE INVENTION

On page 11, line 1, kindly insert the following:

--Table 1--

On page 11, kindly replace Table 1 with the following new Table 1.

	Comparison	Example
	2.A	2.1
in the kneader mixed:		
Buna VSL 5025-1 (37.5 phr mineral oil extended L-SBR, Bayer AG)	61[.].9	61[.].9
natural rubber	10	10
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silica Vulkasil S (Bayer AG)	70	70
silane Si (69 (Degussa Hüls)	6	6
carbon black Corax N121 (Degussa Hüls)	10	10
zinc oxide	3	3
stearic acid	1	1
protective wax Antilux 654 (Rheinchemie)	1[.].5	1[.].5
antioxidant Vulkanox HS (Bayer AG)	1	1
antioxidant Vulkanox 4020 (Bayer AG)	1	1

On the mill admixed

N-cyclohexylmercaptobenzthiazolsulfenamide

Vulkacit CZ (Bayer AG)	1[.].8	1[.].8
diphenylguanidine Vulkacit D (Bayer AG)	2	2
sulfur	1[.].5	1[.].5

On page 12, line 1, kindly insert the following:

--Table--

On page 12, kindly replace Table 2 with the following new Table 2.

	Comparison	Example
	2.A	2.1
tensile strength (Mpa)	16[,] ₁ 8	18[,] ₁ 2
elongation at break (%)	450	330
modulus at 100%	2[,] ₁ 4	2[,] ₁ 9
modulus at 300% elongation (Mpa)	9[,] ₁ 5	16[,] ₁ 3
rebound elasticity at 70°C (%)	54	63
hardness (shore A)	66	66
tan delta at 70°C	0[,] ₁ 138	0[,] ₁ 108

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IN THE CLAIMS:

Kindly cancel Claims 1 - 5.

Kindly add the following new Claims:

- 6. A rubber mixture comprising one or more rubbers with 0.1 to 2 wt.% of bonded carboxyl groups or their salts and a glass transition temperature in the range from -120° to -50°C and one or more fillers in the range 10 to 500 parts by wt., with respect to 100 parts by wt. of rubber.
7. A rubber mixture according to Claim 1, wherein said rubber is formed from diolefins.
8. A process for preparing a rubber with 0.1 to 2 wt.% of bonded carboxyl group comprising the step, after polymerization in solution, of reacting rubber with carboxylmercaptans of the general formula (I)



in which

R¹ represents a linear, branched or cyclic C₁-C₃₆ alkylene group, which may optionally be substituted with up to 3 further carboxyl groups, or which may be interrupted by nitrogen, oxygen or sulfur atoms, or a C₆-C₁₂-arylene group

and

X represents hydrogen or a metal or ammonium ion,

optionally in the presence of radical starters.

9. Molded items comprising rubber mixtures which comprise one or more rubbers with 0.1 to 2 wt.% of bonded carboxyl groups or their salts and a glass transition temperature in the range from -120° to -50°C and one or more fillers in the range 10 to 500 parts by wt., with respect to 100 parts by wt. of rubber.
10. Tires comprising rubber mixtures which comprise one or more rubbers with 0.1 to 2 wt.% of bonded carboxyl groups or their salts and a glass transition temperature in the range from -120° to -50°C and one or more fillers in the range 10 to 500 parts by wt., with respect to 100 parts by wt. of rubber.--

ABSTRACT OF THE DISCLOSURE

The present invention relates to rubber mixtures containing diene rubber with a concentration of carboxyl groups of 0.1 to 2 wt.% and a glass transition temperature of -120 to -50°C and their mixtures with fillers, optionally further rubbers and rubber auxiliary substances and vulcanisates prepared therefrom. Rubber mixtures according to the invention are suitable for producing highly reinforced, abrasion-resistant moulded items, in particular for producing tire treads which have a particularly high resistance to wet skidding, a high abrasion resistance and a low rolling resistance and also for tire sidewalls with especially good fatigue resistance.

1997-1998		1998-1999		1999-2000		2000-2001		2001-2002		2002-2003		2003-2004		2004-2005		2005-2006		2006-2007		2007-2008		2008-2009		2009-2010		2010-2011		2011-2012		2012-2013		2013-2014		2014-2015		2015-2016		2016-2017		2017-2018		2018-2019		2019-2020		2020-2021		2021-2022		2022-2023		2023-2024		2024-2025		2025-2026		2026-2027		2027-2028		2028-2029		2029-2030		2030-2031		2031-2032		2032-2033		2033-2034		2034-2035		2035-2036		2036-2037		2037-2038		2038-2039		2039-2040		2040-2041		2041-2042		2042-2043		2043-2044		2044-2045		2045-2046		2046-2047		2047-2048		2048-2049		2049-2050		2050-2051		2051-2052		2052-2053		2053-2054		2054-2055		2055-2056		2056-2057		2057-2058		2058-2059		2059-2060		2060-2061		2061-2062		2062-2063		2063-2064		2064-2065		2065-2066		2066-2067		2067-2068		2068-2069		2069-2070		2070-2071		2071-2072		2072-2073		2073-2074		2074-2075		2075-2076		2076-2077		2077-2078		2078-2079		2079-2080		2080-2081		2081-2082		2082-2083		2083-2084		2084-2085		2085-2086		2086-2087		2087-2088		2088-2089		2089-2090		2090-2091		2091-2092		2092-2093		2093-2094		2094-2095		2095-2096		2096-2097		2097-2098		2098-2099		2099-2100		2100-2101		2101-2102		2102-2103		2103-2104		2104-2105		2105-2106		2106-2107		2107-2108		2108-2109		2109-2110		2110-2111		2111-2112		2112-2113		2113-2114		2114-2115		2115-2116		2116-2117		2117-2118		2118-2119		2119-2120		2120-2121		2121-2122		2122-2123		2123-2124		2124-2125		2125-2126		2126-2127		2127-2128		2128-2129		2129-2130		2130-2131		2131-2132		2132-2133		2133-2134		2134-2135		2135-2136		2136-2137		2137-2138		2138-2139		2139-2140		2140-2141		2141-2142		2142-2143		2143-2144		2144-2145		2145-2146		2146-2147		2147-2148		2148-2149		2149-2150		2150-2151		2151-2152		2152-2153		2153-2154		2154-2155		2155-2156		2156-2157		2157-2158		2158-2159		2159-2160		2160-2161		2161-2162		2162-2163		2163-2164		2164-2165		2165-2166		2166-2167		2167-2168		2168-2169		2169-2170		2170-2171		2171-2172		2172-2173		2173-2174		2174-2175		2175-2176		2176-2177		2177-2178		2178-2179		2179-2180		2180-2181		2181-2182		2182-2183		2183-2184		2184-2185		2185-2186		2186-2187		2187-2188		2188-2189		2189-2190		2190-2191		2191-2192		2192-2193		2193-2194		2194-2195		2195-2196		2196-2197		2197-2198		2198-2199		2199-2200		2200-2201		2201-2202		2202-2203		2203-2204		2204-2205		2205-2206		2206-2207		2207-2208		2208-2209		2209-2210		2210-2211		2211-2212		2212-2213		2213-2214		2214-2215		2215-2216		2216-2217		2217-2218		2218-2219		2219-2220		2220-2221		2221-2222		2222-2223		2223-2224	
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- 1 -

JC10 Rec'd PCT/PTO 02 NOV 2001

Carboxyl group-containing diene rubbers

5 The present invention provides rubber mixtures which contain a diene rubber with a concentration of carboxyl groups of 0.1 to 2 wt.% and a glass transition temperature of -120 to -50° and their mixtures with fillers, optionally other rubbers and rubber auxiliary substances and vulcanisates prepared therefrom. Rubber mixtures according to the invention are suitable for producing highly reinforced, abrasion-resistant moulded items, in particular for producing tire treads which have particularly high wet skidding resistance and abrasion resistance and a low rolling resistance and also for tire sidewalls with especially high fatigue resistance.

10 Double bond-containing anionic polymerised solution rubbers, such as solution polybutadiene and solution styrene/butadiene rubbers, have advantages over the corresponding emulsion rubbers when producing low rolling resistance tire treads. The advantages are based, inter alia, on the ability to control the vinyl content and the glass transition temperature and molecular branching associated therewith. Particular advantages in relation to the wet skidding resistance and rolling resistance of the tires result therefrom in a practical application. Thus, US-A 5 227 425 describes the production of tire treads from a solution SBR rubber and silica. To further improve the properties, numerous methods for modifying the end groups have been developed, as is described in EP-A 334 042, with dimethylaminopropyl-acrylamide or, as described in EP-A 447 066, with silyl ethers. However, due to the high molecular weight of the rubber, the proportion by weight of the end group is small and can therefore have only a small effect on the interaction between filler and rubber molecule. Inter alia, the present invention is intended to provide diene rubbers with a much higher concentration of effective groups for interacting with fillers and with a particularly low glass transition temperature.

US-A 2 662 874 describes the preparation of elastic materials from metal ion cross-linked polymeric carboxylates with a concentration of 0.001 to 0.3 carboxyl equiva-

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lents per 100 g of rubber. The elastic materials mentioned have a very wide range of carboxyl group contents and are unsuitable for the tire application in the present invention due to the inherent sensitivity to hydrolysis of the metal salts.

5 A process for preparing carboxyl group-containing (3.9 to 8.9 wt.% of carboxyl groups) solution polybutadiene rubbers is described, inter alia, in DE-OS 2 653 144. These rubbers have glass transition temperatures which are too high ($> -50^{\circ}\text{C}$) due to the high concentration of vinyl and carboxyl groups and are associated with disadvantageous damping properties and are therefore not a substitute for 1,4-polybutadiene rubber in tire treads and tire sidewalls.

10 Therefore the present invention was intended to provide mixtures of carboxyl group-containing solution rubbers from which tires with improved wet skidding resistance, lower rolling resistance and high mechanical strength and improved abrasion behaviour can be produced.

15 The present invention therefore provides rubber mixtures containing one or more rubbers with a concentration of bonded carboxyl groups or their salts in the range 0.1 to 2 wt.% and with a glass transition temperature in the range -120 to -50°C and one or more fillers in the range 10 to 500 parts by wt. with respect to 100 parts by wt. of rubber.

20 Preferred rubber mixtures according to the invention are those in which the carboxyl group-containing rubber has a concentration of bonded carboxyl groups or their salts of 0.1 to 1 wt.% and a glass transition temperature in the range -120 to -50°C , preferably -120 to -70°C and a concentration of 1,2-bonded diolefins (vinyl content) in the range 0 to 50 wt.%, in particular 1 to 15 wt.% and a cis-1,4-content in the range 30 to 100 wt.%, in particular preferably 90 to 100 wt.% and also has an average molecular weight (number average) of 50 000 to 2 000 000, preferably 100 000 to 1 000 000 and Mooney viscosities ML 1+4 (100°C) of 10 to 200, preferably 30 to 150.

The glass transition temperature can be determined using known methods, e.g. by using DSC (differential scanning calorimetry, rate of heating 20 K/min). The concentration of carboxyl groups can also be determined using known methods such as e.g. titration of the free acid, spectroscopy, elemental analysis, etc.

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Rubbers according to the invention for use in rubber mixtures according to the invention can be prepared preferably by polymerisation using coordination catalysts or by anionic solution polymerisation. Coordination catalysts in this connection are understood to be Ziegler-Natta catalysts, coordination catalysts and monometallic catalyst systems. Coordination catalysts are preferably those based on Ni, Co, Ti or Nd. Catalysts for anionic solution polymerisation are based on alkali or alkaline earth metals such as e.g. n-butyllithium. In addition, known randomised control agents for the microstructure of the polymer may be used. These types of solution polymerisations are known and are described e.g. in I. Franta *Elastomers and Rubber Compounding Materials*; Elsevier 1989, pages 113 - 131 and in Houben-Weyl, *Methoden der Organischen Chemie*, Thieme Verlag, Stuttgart, 1961, vol. XIV/1 pages 645 to 673 or in vol. E20 (1987), pages 114 to 134 and pages 134 to 153.

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The diolefins used according to the invention for polymerisation are 1,3-butadiene, isoprene, 1,3-pentadiene, 2,3-dimethylbutadiene, 1-vinyl-1,3-butadiene and/or 1,3-hexadiene. 1,3-butadiene and isoprene are particularly preferably used.

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The carboxyl groups may be introduced into the rubber either by adding carboxyl-providing compounds, for example CO₂, to metalised solution rubbers or by treating the final rubber with carboxyl group-containing compounds, for example carboxyl group-containing mercaptans, in a subsequent reaction.

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The carboxyl groups are preferably introduced into the rubber after polymerisation of the monomers being used in solution by reacting the polymer obtained, optionally in the presence of radical starters, with carboxylmercaptans of the formula (I)

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in which

- 5 R^1 represents a linear, branched or cyclic $\text{C}_1\text{-C}_{36}$ alkylene group, which may optionally be substituted with up to 3 further carboxyl groups, or which may be interrupted by nitrogen, oxygen or sulfur atoms or a $\text{C}_6\text{-C}_{12}$ -arylene group,

and

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- X represents hydrogen or a metal or ammonium ion.

This process is a further subject of the invention.

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$\text{C}_1\text{-C}_{36}$ alkylene groups are understood to be any linear, cyclic or branched alkylene groups with 1 to 36 carbon atoms which are known to a person skilled in the art, such as methylene, ethylene, n-propylene, i-propylene, n-butylene, i-butylene, t-butylene, n-pentylene, i-pentylene, neo-pentylene, n-hexylene, cyclohexylene, i-hexylene, heptylene, octylene, nonylene, decylene, undecylene and dodecylene.

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Preferred carboxylmercaptans of the formula (I) are thioglycollic acid, 2-mercaptopropionic acid (thiolactic acid), 3-mercaptopropionic acid, 4-mercaptobutyric acid, mercaptoundecanoic acid, mercaptooctadecanoic acid, 2-mercaptosuccinic acid and their alkali and alkaline earth metal or ammonium salts.

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3-mercaptopropionic acid, mercaptobutyric acid, 2-mercaptosuccinic acid 2- and 4-mercaptobenzoic acid and their lithium, sodium, potassium, magnesium, calcium or ammonium salts are particularly preferred. 3-mercaptopropionic acid and its lithium, sodium, potassium, magnesium, calcium or ammonium salts are more particularly preferred.

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In general, reaction of the carboxylmercaptans with the solution rubbers is performed in a solvent, for example hydrocarbons such as pentane, hexane, cyclohexane, benzene and/or toluene, at temperatures of 40 to 150°C in the presence of radical starters, e.g. peroxides such as dilauroyl peroxide, azo-initiators such as azobisisobutyronitrile, benzopinacolsilyl ethers or in the presence of photo-initiators and visible or UV light. Preferred radical starters are diacyl peroxides such as dilauroyl peroxide, didodecanoyl peroxide, di-(3,5,5-trimethylhexanoyl) peroxide and perketals such as 1,1-di-(tert.-butylperoxy)-3,3,5-trimethylcyclohexane, 1,1-di-(tert.-butylperoxy)-cyclohexane and 1,1-di-(tert.-butylperoxy)-butane.

The amount of carboxylmercaptans to be used is governed by the concentration of bonded carboxyl groups or their salts required in the solution rubber being used in the rubber mixtures.

The carboxylate salts may also be prepared after introduction of the carboxylic acids groups into the rubber, by neutralising them.

Suitable fillers for rubber mixtures according to the invention are any fillers which are known to be used in the rubber industry, these including both active and inactive fillers.

The following may be mentioned:

- highly disperse silicas prepared e.g. by precipitation from solutions of silicates or by flame hydrolysis of silicon halides with specific surface areas of 5 - 1000, preferably 20 - 400, m²/g (BET surface area) and with primary particle sizes of 10 - 400 nm. The silicas may also optionally be present as mixed oxides with other metal oxides such as Al, Mg, Ca, Ba, Zn, Zr or Ti oxides;

- synthetic silicates such as aluminium silicate or alkaline earth metal silicates such as magnesium silicate or calcium silicate, with BET surface areas of 20 - 400 m²/g and primary particle diameters of 10 - 400 nm;
- 5 - natural silicates such as kaolin and other naturally occurring silicas;
- glass fibre and glass fibre products (mats, ropes) or glass microbeads;
- metal oxides such as zinc oxide, calcium oxide, magnesium oxide, aluminium oxide;
- metal carbonates such as magnesium carbonate, calcium carbonate, zinc carbonate;
- 10 - metal hydroxides such as e.g. aluminium hydroxide, magnesium hydroxide;
- carbon blacks. The carbon blacks to be used here are prepared by the lamp black, furnace black or channel black processes and have BET surface areas of 20 - 200 m²/g, e.g. SAF, ISAF, HAF, FEF or GPF carbon blacks;
- 15 - rubber gels, in particular those based on polybutadiene, butadiene/styrene copolymers, butadiene/acrylonitrile copolymers and polychloroprene.

20 Highly disperse silicas and/or carbon blacks are preferably used as fillers.

The fillers mentioned may be used individually or as a mixture. In a particularly preferred embodiment, the rubber mixtures contain a mixture of pale-coloured fillers, such as highly disperse silicas, and carbon blacks, as filler, wherein the mixing ratio of pale-coloured fillers to carbon blacks is 0.05 to 20, preferably 0.1 to 10.

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The fillers are then used in amounts in the range 10 to 500 parts by wt., with respect to 100 parts by wt. of rubber. 20 to 200 parts by wt. are preferably used.

Rubber mixtures according to the invention may contain, in addition to one, two, three or more different carboxyl group-containing solution rubbers according to the invention, other rubbers such as natural rubber or also other synthetic rubbers.

- 5 Preferred synthetic rubbers are described, for example, in W. Hoffmann, Kautschuk-technologie, Gentner Verlag, Stuttgart 1980 and I. Franta, Elastomers and Rubber Compounding Materials, Elsevier, Amsterdam, 1989. They include, inter alia,

	BR	polybutadiene
10	ABR	butadiene/C ₁ -C ₄ -alkyl acrylate copolymers
	CR	polychloroprene
	IR	polyisoprene
	SBR	styrene/butadiene copolymers with styrene contents of 1-60, preferably 20-50 wt. %
15	IIR	isobutylene/isoprene copolymers
	NBR	butadiene/acrylonitrile copolymers with acrylonitrile contents of 5-60, preferably 10-40 wt. %
	HNBR	partially hydrogenated or fully hydrogenated NBR rubber
	EPDM	ethylene/propylene/diene copolymers

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and mixtures of these rubbers. For producing vehicle tires, natural rubber, emulsion SBR and solution SBR rubbers with a glass transition temperature above -50°C, which may optionally be modified with silyl ethers or other functional groups, e.g. according to EP-A 447 066, polybutadiene rubber with a high 1,4-cis content (>90
25 %), which has been prepared using catalysts based on Ni, Co, Ti or Nd, and polybutadiene rubber with a vinyl content of up to 75 % and their mixtures are of particular interest.

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Rubber mixtures which are quite specifically preferred according to the invention contain, in addition to one or more carboxyl group-containing rubbers with a glass transition temperature between -110° and -50°C, additional rubbers chosen from the

group consisting of natural rubber, polyisoprene and styrene/butadiene copolymers with styrene contents between 10 and 50 wt.%. The amount of these additional rubbers is usually in the range 0.5 to 95, preferably 40 - 90 wt.%, with respect to the entire amount of rubber in the rubber mixture. The amount of these additionally
5 added rubbers is again governed by the particular intended use of the rubber mixtures according to the invention.

Obviously, rubber mixtures according to the invention may also contain other rubber auxiliary substances which are used, for example, to cross-link the vulcanisates produced from the rubber mixtures or which improve the physical properties of the vulcanisates produced from rubber mixtures according to the invention for a specific
10 ultimate use.

Sulfur or sulfur-providing compounds, and also radical-providing cross-linking agents such as organic peroxides may be used, for example, as cross-linking agents. Sulfur is preferably used as a cross-linking agent. In addition, as mentioned above, rubber mixtures according to the invention may contain further auxiliary substances such as known reaction accelerators, antioxidants, thermal stabilisers, light stabilisers, anti-ozonants, processing aids, plasticisers, tackifiers, blowing agents, colorants, pigments, waxes, extenders, organic acids, delaying agents, metal oxides and
15 20 activators.

The rubber auxiliary substances according to the invention are used in conventionally disclosed amounts, wherein the amount used is governed by the later ultimate use of the rubber mixtures. Amounts of rubber auxiliary substances in the range 2 to 70 parts by wt., with respect to 100 parts by wt. of rubber, are, for example, conventionally used.
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In the case of rubber mixtures according to the invention which are filled with highly active silicas, the use of additional filler activators is particularly advantageous. Preferred filler activators are sulfur-containing silyl ethers, in particular bis-(tri-
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alkyloxysilyl-alkyl)-polysulfides, as are described in DE 2 141 159 and DE 2 255 577. In addition, oligomers and/or polymers of sulfur-containing silyl ethers corresponding to the description in DE 4 435 311 and EP 670 347 are also suitable. Mercaptoalkyltrialkoxysilanes, in particular mercaptopropyltriethoxysilane and thio-
5 cyanatoalkyl silyl ethers (see DE 19 544 469) may also be used. The filler activators are used in conventional amounts, i.e. in amounts of 0.1 to 15 parts by wt., with respect to 100 parts by wt. of rubber.

Rubber mixtures according to the invention may be prepared, for example, by mixing
10 the carboxyl group-containing solution rubber with the corresponding fillers and optionally further rubbers and further rubber auxiliary substances in appropriate mixing equipment such as compounders, rollers or extruders.

Rubber mixtures according to the invention are preferably prepared by first polymerising the monomers mentioned in solution, introducing the carboxyl groups into
15 the solution rubber and, after completing polymerisation and introduction of the carboxyl groups, mixing the solution rubber in the corresponding solvent with the appropriate fillers and optionally further rubbers and further rubber auxiliary substances, in particular plasticisers, in appropriate amounts, and then removing the solvent with hot water and/or steam at temperatures of 50 to 200°C, preferably under
20 vacuum.

The invention also provides use of the rubber mixtures according to the invention for producing moulded items of all types, in particular for producing tires, especially tire
25 treads and tire sidewalls.

Examples

Example 1

- 5 6.25 of 3-mercaptopropionic acid and 1 g of dilauroylperoxide were added to a solution of 500 g solution polybutadiene rubber, CB 45 NF (Bayer AG, Li-type, cis-1,4-content about 40%) in 4 l cyclohexane at 80°C. The mixture was then stirred for 7 hours at 80°C. Then 2,5 antioxidant Vulkanox 4020 (Bayer AG) and 101.3 g aromatic mineral oil Enerthene 1849-1 (BP) were added and the solvent was distilled off
- 10 using steam (100-110°C). After drying at 70°C under vacuum, 593 g of rubber extended with 20 phr mineral oil were obtained. Sulfur content 0.3 wt%, carboxyl group content 0.5 wt% (based on rubber), viscosity ML 1+4 (100°C) 59, cis-1,4-content 40%, glass transition temperature: -88°C.

15 Example 2:

The following rubber mixtures were prepared in a 1.5 l kneader (mixing time 5 minutes, ejection temperature 150°C). Sulfur and accelerator were admixed afterwards on a mill (50°C):

Comparison 2.A Example 2.1

in the kneader mixed:

Buna VSL 5025-1 (37,5 phr mineral oil extended L-SBR, Bayer AG)

	61,9	61,9
natural rubber	10	10
polybutadiene rubber Buna CB 45 (Bayer)	45	0
carboxylic group containing BR according example 1 (20 phr oil content)	0	54
mineral oil Enerthene 1849-1 (BP)	20	11
silica Vulkasil S (Bayer AG)	70	70
silane Si (69 (Degussa Hüls)	6	6
carbon black Corax N121 (Degussa Hüls)	10	10
zinc oxide	3	3
stearic acid	1	1
protective wax Antilux 654 (Rheinchemie	1,5	1,5
antioxidant Vulkanox HS (Bayer AG)	1	1
antioxidant Vulkanox 4020 (Bayer AG)	1	1

On the mill admixed

N-cyclohexylmercaptobenzthiazolsulfenamide

Vulkacit CZ (Bayer AG)	1,8	1,8
diphenylguanidine Vulkacit D (Bayer AG)	2	2
sulfur	1,5	1,5

The rubber mixtures were subsequently vulcanized at 170°C for 15 minutes. The following vulcanisate properties were obtained.

	Comparison 2.A	Example 2.1
tensile strength (Mpa)	16,8	18,2
elongation at break (%)	450	330
modulus at 100%	2,4	2,9
modulus at 300% elongation (Mpa)	9,5	16,3
rebound elasticity at 70°C (%)	54	63
hardness (shore A)	66	66
tan delta at 70°C	0,138	0,108

The experimental data confirm the significant lower dynamic damping at 70°C, measured by rebound elasticity and tan delta, which in practice correlates with a significantly reduced rolling resistance in tires.

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Example 3:

Preparing a masterbatch from precipitated silica and carboxyl group-containing BR rubber:

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Using the method in example 1, 500 g of BR rubber Buna CB 65 in 4 l of cyclohexane at 80°C were reacted with 12.5 g of 3-mercaptopropionic acid and 0,5 g of dilauryl peroxide. Reaction time: 5 hours. At this point 36% of the 3-mercaptopropionic acid had reacted. The carboxyl group content of the polymer was 0.38 wt.%. Then, with stirring at 75°C, 2.5 g of stabiliser Vulkanox® 4020 (Bayer AG), 189.5 g of aromatic mineral oil Renopal® 450 (Fuchs Mineralölwerke) and 405 g of highly active precipitated silica Vulkasil® S (N₂ surface area about 180 m²/g, Bayer AG) were added and the mixture was stirred for about 30 minutes at this temperature until these components were uniformly distributed. The solvent was then removed by passing steam (100-110°C) through the mixture. The reaction vessel was heated to 75-80°C from outside during this procedure. Finally, the moist solid was removed, finely divided silica was filtered off through a sieve, and the product was dried at 65°C under

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vacuum. 1090 g of a brown silica/rubber masterbatch (99 % of theoretical) were obtained. The waste water contained no silica.

Comparison example 3.A:

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The same procedure was used as described in example 3, wherein a solution of 500 g of BR rubber Buna CB 65 and 2.5 g of Vulkanox[®] 4020 in 4 l of cyclohexane were mixed at 75°C with 400 g of highly active silica Vulkasil[®] S. The solvent was then removed by passing steam (100-110°C) through the mixture, wherein the reaction

10 vessel was heated to 75-80°C from outside. Finally, the moist solid was removed, finely divided silica was filtered off through a sieve and the product was then dried at 65°C under vacuum. 597 g (66 % of theoretical) of an inhomogeneous silica/rubber masterbatch were obtained. The waste water contained large amounts (about 75 % of the amount used) of silica.

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Claims

1. A rubber mixture containing one or more rubbers with in the range of 0.1 to 2
5 wt.% of bonded carboxyl groups or their salts and a glass transition temperature in the range from -120° to -50°C and one or more fillers in the range 10 to 500 parts by wt., with respect to 100 parts by wt. of rubber.
2. A rubber mixture according to Claim 1, characterised in that the rubber is
10 built up from diolefins.
3. A process for preparing a rubber with in the range of 0.1 to 2 wt.% of bonded
carboxyl groups, characterised in that, after polymerisation in solution, the
15 rubber is reacted with carboxylmercaptans of the general formula (I)



in which

- 20 R^1 represents a linear, branched or cyclic $\text{C}_1\text{-C}_{36}$ alkylene group, which may optionally be substituted with up to 3 further carboxyl groups, or which may be interrupted by nitrogen, oxygen or sulfur atoms, or a $\text{C}_6\text{-C}_{12}$ -arylene group

25 and

X represents hydrogen or a metal or ammonium ion,

optionally in the presence of radical starters.

30

ATTORNEY DOCKET NO

DIENE RUBBERS CONTAINING CARBOXYL GROUPS

as a PCT Application Serial No. **PCT/EP00/03618**

Prior Foreign Application(s), the priority(ies) of which is/are to be claimed:

May 6, 1999
(Month/Day/Year Filed)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose the material information as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(patented, pending, abandoned)

(patented, pending, abandoned)

Le A 33 677-US

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